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In re application of: Bose, et al.

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For: METAL-COATED CARBON SURFACES FOR USE IN FUEL CELLS

Attorney Docket No: 2384.00059

Assistant Commissioner for Patents
Washington, D.C. 20231

DECLARATION

I, Dr. Rathindra N. Bose, being duly sworn, do hereby state that:

1. I am a co-inventor of the above-captioned application.

2. I am skilled in the art and have worked extensively in the field of electrocatalytic reduction and fuel cells.

3. The claims have been rejected for both containing new matter and being anticipated by U.S. Patent No. 5,284,571 to Verbrugge. With regard to the new matter rejections, Figure 2 of the present invention shows that the only possible method of applying the metal complex on the carbon article is through reductive electropolymerization. One skilled in the art would certainly recognize that this process was used, not conventional cyclic voltammetry, and thus amending the specification to describe what is evident in the Figure is not new matter.

The claims in the current application have nothing to do with cyclic voltammetry, but pertain to the invention of a new method for uniform coating of a metal surface onto a substrate, a carbon article for example, by reductive electropolymerization. The cyclic voltammetric technique was discovered more than a century ago, and was neither the discovery by Verbrugge nor by the inventors of the present invention. Verbrugge deposited platinum metal on carbon article from platinum salts by conventional electrodeposition, i.e., applying voltage to reduce

platinum(II) to platinum metal. The range of voltage selection, voltage cycling, scan speed, etc. are all part of the conventional cyclic voltammetry techniques, not Verbrugge's discovery. The current application deals with the electropolymerization of a metal complex on a carbon support to layout a uniform coating first by applying voltage and then by reducing the complex to metal on to the surface.

The evidence for electropolymerization is clearly displayed in Figure 2. Skilled workers in the field would immediately conclude the existence of electropolymerization based on the features of current-voltage in repeated cycles displayed in Figure 2. Many electrochemists have published similar features as displayed in Figure 2 as the clear evidence for electropolymerization. Two articles on the vast literature on electropolymerization, Abruna et al. (Journal of the American Chemical Society, 1981, vol 103, 1-5, and Gurr & Anson (J. Phys. Chem. 1987, vol 91, 4037-4043) are attached where several diagrams similar to Figure 2 are displayed as the evidence for electropolymerization.

The claims have been amended to reflect the unique properties of reductive electropolymerization. A polymerizable metal is required to be used, and a step-wise increase in current is effected until the polymerizable metal is saturated on the carbon article. Such a step-wise increase in current does not occur with conventional cyclic voltammetry. The only possible way that this increase would occur, as described in the previously submitted Declaration, would be through electropolymerization. In other words, Figure 2 of the present invention cannot show another process besides electropolymerization, and thus the amendments to the claims and specification are obvious corrections.

Verbrugge discloses conventional cyclic voltammetry which is unlike the process of electropolymerization in the present invention. Verbrugge discloses three methodologies to electrodeposit metal by using positively charged metal species. The abstract of Verbrugge clearly states that "The method of the invention deposits positively charged metal species, preferably platinum-ammine, at sites where negatively charged sulfonic acid groups of the SPE are in contact with carbon". These methodologies are then elaborated by providing three examples. In example 1, 0.01 M $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ (a cationic complex) was used by setting a potential at -2 V vs. Ag/AgCl electrode. In example 3, Verbrugge deposited platinum on a glassy carbon

surface by rotating disk method with a rotating speed of 1000 rotations per minute by scanning potential from 0 to -0.8 V. Example 3 in Verbrugge's invention was used to document that these electrodeposited materials show hydrogen evolution at potential more negative than -1 V, breakdown of solvent at low metal concentrations, and pointed out the limitation of the use of low concentration of metal cation for electrodeposition. In example 4, a -0.75 V fixed potential was used to electrodeposit platinum again from cationic 10 mM $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ solution. In fact, half an hour deposition yielded only 0.1 mg/cm² platinum. In other words, Verbrugge discloses conventional electrodeposition through rotating disk electrode voltammetry, and controlled potential electrolysis.

In contradistinction, the present invention requires the use of cyclic voltammetry to electrocatalyze polymerization (i.e. electropolymerization) of anionic, cationic, or neutral platinum complexes on carbon substrates followed by reduction (reductive electropolymerization) to form a uniform thin-film of metal with variable loadings from 0.03 mg/cm² to 0.2 mg/cm². Applicants have amended the presently pending claims to more accurately describe the invention, i.e. coating a carbon article with a polymerizable metal by reductively electropolymerizing the polymerizable metal on the carbon article through cyclic voltammetry, and forming a polymerized metal coating on the carbon article by effecting a step-wise increase in current until the polymerizable metal is saturated on the carbon article. The technique of cyclic voltammetry has long been known to electrochemists; however, Applicants have used herein a nonconventional method that was previously not expected to work. Applicants used this technology to electrocatalyze platinum metal complexes to form polymeric species to uniformly coat carbon substrate followed by reduction to make a thin-film. This technique is characterized by a large jump in current, i.e. **a step-wise increase in current is effected until the polymerizable metal is saturated on the carbon article**, as demonstrated in Figure 2 and further explained below. This step is not present in Verbrugge.

Although, the present application did not specifically use the terminology "electrocatalyzed polymerization" or "electropolymerization", it should be obvious to one skilled in the art from the body of the figures, data, and evidence provided in the present application that the methodology is not conventional electrodeposition by conventional voltammetry as described in Verbrugge, but rather electrocatalyzed

polymerization followed by reduction. Thus, Applicants have amended the claims and specification to more accurately describe the invention, without adding any new matter, as the modifications were inherently present to one skilled in the art.

For example, Figure 2 in the present application clearly demonstrates the deposition technique is based on electrocatalysis leading to polymerization of platinum complexes on carbon surfaces. In this Figure, the increase in peak current in successive cycles, as indicated by cycles 1, 2, 3 etc., shows dramatic increase in current compared to latter cycles. There is no reduction peak at -0.7 V for the first cycle, the distinct formation of the reduction peak became visible in cycle 3. This peak is due to formation a thin uniform platinum film due to electropolymerization which is the active electrocatalyst. This modified carbon surface coated with platinum thin film is the active electrode for the reduction of phosphate blue used in Figure 2 since a carbon electrode alone does not reduce the phosphate blue species.

For conventional electrodeposition of platinum, one would expect a slow growth in peak at -0.7 V, and the current in successive cycles would depend on the bulk concentration of the platinum phosphate complex. Therefore, the change in the magnitude of current between two successive cycles would either be constant (where the changes in bulk concentration of platinum complex in solution is negligible due to small amount of electrodeposition) or less due to the depletion of the substrates. This is due to the fact that the current in cyclic voltammetry, or linear voltammetry, linearly depends on the concentration of the electro-active species and square root of the scan speed as listed in the patent application.

Furthermore, when a thin-film formation is complete in the present invention, very little changes in peak current at -0.7 V were apparent beyond 5th cycle, confirming the behavior of microelectrode in cyclic voltammetry that no further changes in the electrode surface were taking place and that the bulk electro-active species is quasireversibly reduced and oxidized without significantly depleting its concentration. The above observations can only be described by a process in which platinum complexes in solution were polymerized at the carbon surface and then were reduced to platinum on the same surface by application of potential. Once carbon surface is covered with a platinum thin-film, such polymerization no longer

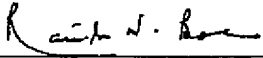
takes place since no changes in the voltammograms were observed. Therefore, **this process can best be described by reductive electropolymerization.** Applicants have amended the independent claims to require a polymerizable metal and that the step-wise increase in current is effected until the polymerizable metal is saturated on the carbon article. These characterizing features of reductive electropolymerization are not present in Verbrugge. In fact, following the submission of the present patent application, Applicants have published an article entitled, "Electrocatalytic reduction of platinum phosphate blue on carbon surfaces: A novel method for preparing fuel cell electrode" which appeared in the Journal of Power Sources, 2006, vol.157, pp188-192 (previously submitted). See page 191 of the Discussion regarding reductive polymerization.

There are further differences between Verbrugge and the present invention. The present invention's electropolymerization can be applied to anionic complexes whereas Verbrugge only discloses cationic complexes; two such examples are shown in Table 1 in the application, $\text{Pt}_2(\text{NH}_3)_2(\text{PO}_4)_2^{2-}$ and PtCl_4^{2-} . Applicants used forward scan (cathodic scan) to form thin-films by reductive electropolymerization, and the reverse scans were used to reoxidize any platinum that might have deposited due to conventional electrodeposition. Such conventional electrodeposition by constant current or potential scan is detrimental to the surface. Applicants' technology can be applied in lower concentrations; there is not a low concentration limit. Applicants' methodology is applicable to any complexes (cationic, anionic, or neutral) as long as these complexes can be polymerized at the carbon surfaces.

Therefore, since the Verbrugge patent does not disclose coating a carbon article with a polymerizable metal by reductively electropolymerizing the polymerizable metal on the carbon article through cyclic voltammetry, and forming a polymerized metal coating on the carbon article by effecting a step-wise increase in current until the polymerizable metal is saturated on the carbon article as set forth in the presently pending independent claims, the claims are patentable over the Verbrugge patent and reconsideration of the rejection is respectfully requested.

The undersigned declares further all statements made herein of his knowledge are true and that all statements made upon information and belief are believed to be true, and further that the statements were made with the knowledge that willful and false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: June 16, 2008



Dr. Rathindra N. Bose

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Rectifying Interfaces Using Two-Layer Films of Electrochemically Polymerized Vinylpyridine and Vinylbipyridine Complexes of Ruthenium and Iron on Electrodes

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Contribution from the Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received May 14, 1980

Abstract: Polymerization of the complexes $[\text{Ru}(\text{bpy})_2(\text{vinyl-py})_2]^{2+}$ (I), $[\text{Ru}(\text{vinyl-bpy})_2]^{2+}$ (II), $[\text{Ru}(\text{bpy})_2(\text{vinyl-bpy})]^{2+}$ (III), $[\text{Ru}(\text{bpy})_2(\text{vinyl-py})\text{Cl}]^+$ (IV), and $[\text{Fe}(\text{vinyl-bpy})_2]^{2+}$ (V) can be initiated by electrochemical reduction in CH_3CN solvent to produce stable, adherent, electrochemically active films on Pt, vitreous carbon, SnO_2 , and TiO_2 electrodes. Randomly site-mixed copolymer (one-layer) and spatially segregated two-layer films of the pairs I and IV and II and V can be prepared by simultaneous and sequential polymerization of the appropriate monomers, respectively. The spatial features were confirmed by variable-angle X-ray photoelectron spectroscopy. Cyclic voltammetry of the copolymers is the additive response of the two redox components. In the two-layer films, however, oxidation state changes of the outer polymer films are constrained to occur via electron-transfer mediation by the inner polymer film. The result is a rectifying property of the polymer two-layer interface which should be useful in mimicking electronic device behaviors such as Zener diodes.

Photosensitization and/or anticorrosive protection of semiconductor/solution interfaces, by coatings of electroactive substances, has experienced much research scrutiny, due to potential use in solar energy conversion schemes.¹ The alternate possibility that electrodes coated with electroactive substances might be made to exhibit rectifying properties even through neither the electrode nor the electroactive substance is individually a semiconductor has on the other hand received no attention. We present here the principle and experimental demonstration of a scheme for unidirectional current flow based on a conductor electrode (e.g., Pt) coated with two (or more) physically discrete layers of electroactive materials of different redox potentials. The essence of this two-layer or bilayer scheme² is that electron transfer between the Pt electrode and the outer electroactive layer is forced to occur catalytically, by electron-transfer mediation through redox states of the inner electroactive layer.

Demonstration of the bilayer scheme is based on the polymeric and copolymeric films of fully metalated vinylpyridine and vi-

nylbipyridine complexes of ruthenium and iron, the chemistry of which is introduced here. A more complete report will be presented elsewhere. These films are the first examples of redox-polymer/modified electrodes³ where electrode coatings are made by electrochemically initiating polymerization of metal complex monomers bearing vinyl-substituted ligands, e.g., $[\text{Ru}^{II}(\text{bpy})_2(\text{vinyl-py})_2]^{2+}$ (I) (bpy = 2,2'-bipyridine, vinyl-py = 4-vinylpyridine). Given that (i) in complexes like I there exist π -back-bonding interactions which put some electron density in the ligand π^* orbitals⁴ and that reduction of the complex is ligand rather than metal localized⁵ and that (ii) polymerization of vinylpyridine can be anionically initiated,⁶ we reasoned that electrochemical reduction of I might initiate its polymerization. Not only does polymerization in fact occur but also the electrode used for the reductive initiation rapidly becomes coated with a stable, adherent, nonpassivating, electrochemically active, polymeric film of the complex.

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(2) Although we shall discuss only bilayer electrodes here, the principles presented are readily extended to larger numbers of spatially segregated layers. Our use of the descriptor "bilayer" is not to be taken to mean a double monomolecular layer; here, films are much thicker.

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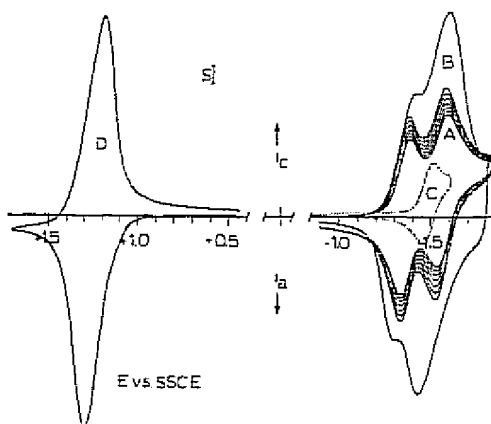


Figure 1. Cyclic voltammograms in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$: Curve A, first seven cyclical potential scans between 0 and -1.8 V vs. SSCE of a Pt electrode in an 0.5 mM solution of I, $S = 5 \mu\text{A}$; curve B, same electrode as curve A, after continuous scanning for 0.5 h and transfer to solution containing no dissolved I, at 1/10 the current sensitivity, $S = 50 \mu\text{A}$; curve C, a solution of dissolved IV, $S = 2.5 \mu\text{A}$; curve D, same electrode as curve B, in absence of dissolved I, scanning in the anodic region, $S = 25 \mu\text{A}$.

This polymerization chemistry seems rather general; related complexes which have been polymerized as films include $[\text{Ru}^{\text{II}}(\text{vinyl-bpy})_3]^{2+}$ (II) (vinyl-bpy = 4-vinyl-4'-methyl-2,2'-bipyridine), $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{vinyl-bpy})]^{2+}$ (III), $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{vinyl-py})\text{Cl}]^+$ (IV), and $[\text{Fe}^{\text{II}}(\text{vinyl-bpy})_3]^{2+}$ (V). Electrode materials employed include platinum, vitreous carbon, and the semiconductors SnO_2 and TiO_2 .

Films prepared by reduction of one of the monomer complexes I–V are homopolymers (one-layer). If an appropriately chosen pair of complexes such as I and IV or II and V is simultaneously reduced, a one-layer copolymer film can be formed. On the other hand, if an electrode coated with a polymer of one complex is used to reduce a different monomer complex in another solution, a polymer of the second monomer forms at the solution boundary of the first polymer layer; i.e., a bilayer film is made. This procedure has been used to prepare bilayer films of the pairs I and IV and of II and V, where I and II are the inner and IV and V the outer polymer layers. These bilayer electrodes will be compared with the corresponding one-layer copolymer electrodes to demonstrate the rectifying characteristic of the bilayer scheme.

Experimental Section

Chemicals. The ligand 4-vinyl-4'-methyl-2,2'-bipyridine (vinyl-bpy) was prepared according to Spiro and Ghosh.⁷ Treatment of 4,4'-dimethyl-2,2'-bipyridine with lithium diisopropylamide generated the α -lithio derivative which was then treated with an excess of dry, gaseous formaldehyde. The resulting 4-(hydroxyethyl)-4'-methyl-2,2'-bipyridine was dehydrated with P_2O_5 to yield the vinyl-bpy species.

A sample of vinyl-bpy employed in early stages of this work was contaminated with ca. 20% (NMR) of the starting material, dimethylbipyridine. The tris(bipyridine) complexes prepared from this sample were thus mixtures of complexes bearing three or fewer vinyl groups. A statistical distribution would be expected to comprise 51% "trivinyl", 38% "divinyl", 10% "monovinyl", and less than 1% unsubstituted (and non-polymerizing) complex. A sample of II subsequently prepared from pure 4-vinyl-4'-methyl-2,2'-bipyridine gave electrode coatings identical with those prepared from the mixture in all discernible aspects.

Ruthenium and iron complexes I–V were prepared following standard procedures^{8–10} (II from RuCl_3 , III from $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, and V from FeSO_4). Under the conditions of preparation, no polymerization of the ligand or complexes has been observed.

Electrochemical solvents were 0.1 M $\text{Et}_4\text{NClO}_4/\text{acetonitrile}$ (both for polymerization and electrochemical measurements) and 1 M H_2SO_4 .

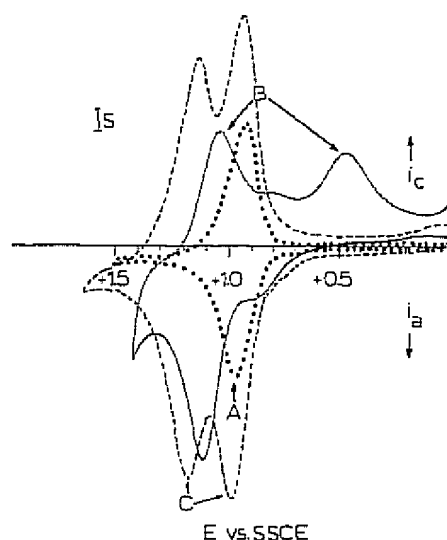


Figure 2. Cyclic voltammograms of polymer films on Pt electrodes: curve A, poly-V in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at 50 mV/s, $S = 10 \mu\text{A}$; curve B, poly-I in 1 M H_2SO_4 at 200 mV/s, $S = 25 \mu\text{A}$; curve C, copolymer of poly-II and poly-V in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at 50 mV/s, $S = 2.5 \mu\text{A}$.

Equipment. Electrochemical potentiostats, triangular wave generators,¹¹ and electrochemical cells were of local and conventional design. Electrochemical potentials are referenced to the NaCl-saturated SCE (SSCE). X-ray photoelectron spectroscopy (XPS) was conducted on a Physical Electronics Industry Model 548 AR spectrometer equipped with a movable slit for electron emission angular distribution measurements.

Results and Discussion

Electrochemically Initiated Polymerization of Vinylpyridine and Vinylbipyridine Complexes. Figure 1A shows the result of cycling the potential applied to a Pt electrode in a 0.5 mM solution of I in 0.1 M $\text{Et}_4\text{NClO}_4/\text{acetonitrile}$ between 0 and -1.8 V vs. SSCE. From the first cycle, the voltammetric waves grow steadily; an insoluble, presumably polymeric form of I accumulates on the Pt surface. Continuous cycling (0.2 V/s) for 30 min followed by transfer of the thoroughly washed electrode to fresh 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ containing no dissolved I yields well-defined reduction (Figure 1B) and oxidation (Figure 1D) waves for the accumulated polymeric I, designated Pt/poly-I. The formal potential for the poly-I, $\text{Ru}^{\text{III/II}}$ step, $E_{\text{surf}}^{\circ} = 1.22$ V vs. SSCE, is close to that of monomer I, 1.24 V, and the charge under this surface wave indicates that the film contains 1.45×10^{-8} mol/cm² of electroactive ruthenium, which is equivalent to approximately 175 monolayers¹² of I in a layer ca. 0.25 μm thick.

The reductive polymerizations of monomers II and V are qualitatively similar to that of Figure 1. An example of the Pt/poly-V electrode, shown in Figure 2A, has $E_{\text{surf}}^{\circ} = 0.935$ V vs. SSCE, which is identical with $E_{\text{soln}}^{\circ} = 0.93$ V for the $\text{Fe}^{\text{III/II}}$ wave of monomeric V. Polymerizations of monomers III and IV as homopolymers also occur but yield lower coverages, probably reflecting the importance of cross-linking afforded by multiple vinyl groups.

Polymerization can be effected at constant as well as with scanned potential, and the quantity of polymer deposited on the electrode is controlled by the time of electrolysis and by the negative potential limit. Thus, in experiments conducted as in Figure 1A, varying the time of potential cycling from 5 to 120 min yields coverages of poly-I ranging from ca. 2×10^{-9} to 1.3×10^{-7} mol/cm² (e.g., ca. 24–1560 monolayers) as measured by the charge under the $\text{Ru}^{\text{III/II}}$ wave. Electrochemical properties

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(11) Woodward, W. S.; Rocklin, R. D.; Murray, R. W. Chem., Biomed. and Environ. Instrum. 1979, 9, 95.

(12) On the basis of packing hard spheres of radius 7.1 Å in a plane, a monomolecular layer of I is estimated as ca. 8.3×10^{-11} mol/cm², in a layer ca. 14.2 Å thick.

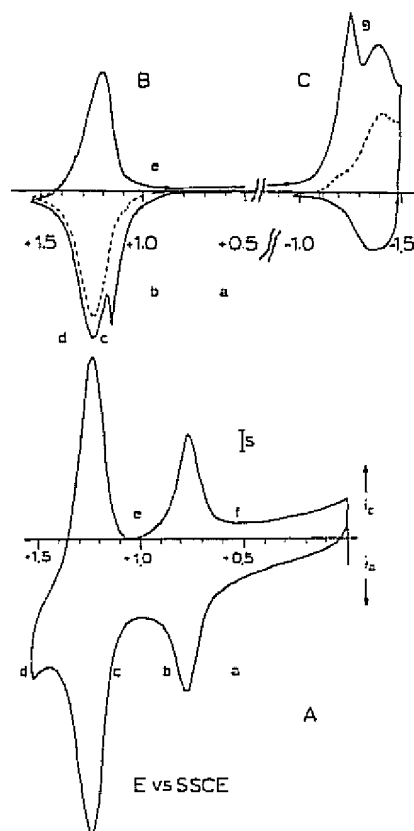


Figure 3. Cyclic voltammograms in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ of copolymer Pt/copoly-I,IV (curve A, 100 mV/s, $S = 0.5 \mu\text{A}$) and two-layer Pt/poly-I/copoly-I,IV (curve b, (—) first scan, (---) second scan, 20 mV/s, $S = 10 \mu\text{A}$; curve C subsequent negative scan, 50 mV/s, $S = 25 \mu\text{A}$). Oxidation states in the films, giving the state of I first, at the lettered potentials (a–g) are as follows: copolymer $\text{Ru}^{\text{II}}, \text{Ru}^{\text{II}}$ (a), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (b), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (c), $\text{Ru}^{\text{III}}, \text{Ru}^{\text{III}}$ (d), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (e), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{II}}$ (f); (—) bilayer $\text{Ru}^{\text{II}}, \text{Ru}^{\text{II}}$ (a), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{II}}$ (b), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (c), $\text{Ru}^{\text{III}}, \text{Ru}^{\text{III}}$ (d), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (e), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (f); (---) bilayer $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (a), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (b), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (c), $\text{Ru}^{\text{III}}, \text{Ru}^{\text{III}}$ (d), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (e), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (f), $\text{Ru}^{\text{II}}, \text{Ru}^{\text{III}}$ (g).

of the films are well-defined over this coverage range; the thicker ($\geq 10^{-8} \text{ mol/cm}^2$) films show larger ΔE_{peak} values and broadened waves. Polymerization of I also proceeds, but more slowly, at potentials confined to the first monomer reduction wave only (e.g., -1.37 V). On the other hand, potentials oxidizing monomer I to the Ru^{III} state or simple exposure of the Pt surface to a solution of I does not result in polymeric accumulation of I on the Pt surface.¹³ These results show that polymerization and electrode deposition is most favored by a highly reduced form of the complex, which is consistent with (but does not prove) the hypothesis (vide supra) associating a ligand-centered reduction with anionic polymerizability of 4-vinylpyridine.

The electrochemical polymerization mechanism has chain propagation character. A Pt electrode at -1.4 V vs. SSCE in a solution of IV accumulates no polymer on the surface; this potential is insufficient to reduce IV ($E_{\text{red}}^{\text{IV}} = -1.49 \text{ V}$, Figure 1C). Monomer I, however, does form a polymer film at -1.4 V . A Pt electrode in a solution of 0.08 mM in I and 0.25 mM in IV to which a potential of -1.4 V vs. SSCE is applied for 120 min, reducing only the smaller concentration of I, nonetheless incorporates a significant quantity of IV into the film as a copolymer constituent. See the Pt/copoly-I,IV film voltammogram in Figure 3A. In fact, formation of polymeric films of IV is aided by addition of a small concentration of I to the monomer solution, forming the

copolymer film by reducing I at -1.4 V .

While our stability experiments are not exhaustive, these polymer films seem very durable to repeated potential cycling, and are stable and remain electroactive in other solvents such as CH_2Cl_2 and $1 \text{ M H}_2\text{SO}_4$. In $1 \text{ M H}_2\text{SO}_4$, for example, no measurable change in the $\text{Ru}^{3+}/^{2+}$ wave results from continuously cycling a Pt/poly-I electrode between -0.2 and 1.4 V vs. SSCE for 15 min or from soaking in the same solution for 16 h. Interestingly, the cyclic voltammogram in this case¹⁴ shows, in addition to the $\text{Ru}^{\text{III}}/\text{II}$ polymer surface wave, the platinum oxide forming and stripping waves (Figure 2B). It is striking that oxide films can be formed and reduced repeatedly at the interface between the platinum and the polymer films without adverse effect on either the polymer's charging rate or stability. The ability to generate a stable polymer film containing $[\text{Ru}(\text{bpy})_3]^{3+}$ -like states in aqueous media is an important and encouraging result.

Immobilization of ruthenium complexes with highly oxidizing redox potentials on electrode surfaces has been actively pursued once it was recognized that such complexes could act as photosensitizers in solar energy conversion schemes.¹⁵ Such complexes have also attracted interest because, on *n*-type semiconductors undergoing bandgap absorption, they could serve as electron-transfer mediators with greater oxidizing power than the presently used ferrocenes.¹⁶ The complex $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ is particularly attractive, having a high oxidation potential ($E_{\text{ox}}^{\text{Ru}^{\text{II}}/\text{III}} = 1.29 \text{ V}^{17}$ and 1.02 V^{18} vs. SSCE in $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ and $1 \text{ M H}_2\text{SO}_4$, respectively), being chemically robust, and having an unusually long-lived ($\tau \approx 0.6 \mu\text{s}$) charge-transfer excited-state $[\text{Ru}(\text{bpy})_3]^{2+*}$ thermodynamically capable^{19,20} both of oxidizing water to oxygen and of reducing it to hydrogen at pH 7.

With this in mind and since the monomers I and II are close structural analogues of $[\text{Ru}(\text{bpy})_3]^{2+}$, it was of interest to see whether polymeric films of these complexes could be deposited on *n*-type semiconductors. Since the flat band potentials of SnO_2 and TiO_2 in acetonitrile are both less negative than the potentials required to reduce I and II making their behavior metal-like in this potential region, deposition of polymeric films proved to be straightforward. These coated materials are being further studied.

Films deposited on Pt and on optically transparent SnO_2 are visibly colored, golden to orange, depending on thickness, and optical spectra of the polymers can be employed in their analysis. A spectrum of a polymer film of I on optically transparent tin oxide for example exhibits $\lambda_{\text{max}} = 438 \text{ nm}$ in acetonitrile which agrees with $\lambda_{\text{max}} = 432 \text{ nm}$ for dissolved monomer I. Elemental analysis of a sample of poly-I harvested from a thick coating on SnO_2 furthermore agrees with the expected stoichiometry.²¹ These results plus the agreement of poly-I and monomer I formal potentials indicate that the ruthenium coordination sphere remains essentially intact upon polymerization and that poly-I can be regarded as nearly if not fully metalated. This latter aspect is of interest since attempts at binding metals to preformed polymer ligand backbones typically result in incomplete metalation.^{3a,22}

(14) In Figure 2B, the waves at $E_{\text{pa}} = +0.88$ and $E_{\text{pc}} = +0.49 \text{ V}$ are associated with platinum oxide formation and reduction, respectively, while those at $E_{\text{pa}} = +1.14 \text{ V}$ and $E_{\text{pc}} = +1.05 \text{ V}$ are associated with the film of poly-I. The identity of the wave at $E_{\text{pc}} = +0.80 \text{ V}$ is unknown.

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(20) $[\text{Ru}(\text{bpy})_3]^{2+*}$ ($E^* = +0.84 \text{ V}$ vs. NHE), $[\text{Ru}(\text{bpy})_3]^{2+*}$ ($E^* = -0.84 \text{ V}$ vs. NHE). The redox properties of this system can be further enhanced by ca. 0.4 V by oxidative or reductive quenching to give $[\text{Ru}(\text{bpy})_3]^{3+}$ ($[\text{Ru}(\text{bpy})_3]^{3+}/^{2+}$, $E^{\text{ox}} = 1.29 \text{ V}$) or $[\text{Ru}(\text{bpy})_3]^{1+}$ ($[\text{Ru}(\text{bpy})_3]^{1+}/^{2+}$, $E^{\text{red}} = -1.32 \text{ V}$), respectively, see: (a) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* 1979, 101, 4815; (b) Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. *Ibid.* 1977, 99, 1980; (c) Maestri, M.; Graetzel, M. *Ber. Bunsenges. Phys. Chem.* 1977, 81, 504; (d) Mulazzani, Q. G.; Emmi, S.; Fucchi, P. G.; Hoffman, M. E.; Venturi, M. *J. Am. Chem. Soc.* 1978, 100, 981; Whitten, D. G. *Acc. Chem. Res.* 1980, 13, 83.

(21) Calcd: C, 49.6; N, 10.21; H, 3.65. Found: C, 49.3; N, 9.45; H, 3.49.

(13) If a Pt electrode is immersed in an acetonitrile solution of $[\text{Ru}(\text{bpy})_2(\text{vinyl-py})_2]^{2+}$ for 4 h, some bonding occurs ($< 3 \times 10^{-11} \text{ mol/cm}^2$), presumably by interaction of the vinyl groups with the Pt surface.

We should note that the present ruthenium polymer films differ from those described by Oyama and Anson^{3a} in having a pre-formed monomer and thus a well-defined metal coordination in the polymer film. In addition, these films are probably cross-linked and thus insoluble in a range of solvents, are amenable to copolymerization, and achieve high oxidation potentials similar to $[\text{Ru}(\text{bpy})_3]^{3+}$. With the synthetic versatility afforded by the monomer $[\text{Ru}(\text{vinyl-bpy})_2\text{Cl}_2]$ (by analogy to $[\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}]$), we hope to prepare copolymer films, with an array of formal potentials, which would serve as generalized outer-sphere electrocatalysts. Studies along this line are being pursued.

The Bilayer Scheme. When a pair of monomer metal complexes is simultaneously reduced to form a randomly mixed one-layer copolymer, the two types of monomer sites exhibit independent, facile electron-transfer reactions with the underlying electrode at the expected potentials.²³ This is demonstrated for a one-layer copolymer of II and V made by cycling the potential between 0.0 and -1.8 V vs. SSCE in an equimolar solution of monomers II and V in Figure 2C.

Consider now a bilayer electrode made from monomers I and IV by (i) potentiostatting a Pt electrode at -1.75 V vs. SSCE in 0.3 mM I for 60 min, (ii) washing, and (iii) potentiostatting this surface at -1.4 V in 0.017 mM I plus 0.25 mM IV for 60 min, all in 0.1 M $\text{Et}_4\text{ClO}_4/\text{CH}_3\text{CN}$. In (iii) the small amount of I facilitates polymerization of IV, forming an outer film copolymer, so the bilayer electrode is most precisely designated Pt/poly-I/copoly-I,IV.²⁴ Cyclic voltammetry of this bilayer electrode (Figure 3B) is strikingly different from the corresponding one-layer copolymer (Figure 3A). The "truth table" in the figure legend compares bilayer and one-layer copolymer ruthenium oxidation states at the indicated potentials. In the bilayer film, the (outer-film)-poly-IV sites, isolated from the Pt, are not oxidized at potential b. Instead, when potentials (c) generating a small population of Ru^{III} sites in the inner poly-I film are attained, $(\text{Ru}^{\text{II}})\text{poly-IV}$ sites are oxidized by these through catalytic electron-transfer mediation at the poly-I-poly-IV interface. The inner-film-mediated oxidation of the outer film typically occurs as a sharp prewave,²⁵ which is followed by a wave for oxidation of the rest of the inner film $(\text{Ru}^{\text{II}})\text{poly-I}$ sites. At potential d, the bilayer film is fully oxidized (all Ru^{III}).

When the potential scan is reversed, a current peak for reduction of Ru^{III} sites in the inner film (i.e., $(\text{Ru}^{\text{III}})\text{poly-I}$) is observed (Figure 3B), but the $(\text{Ru}^{\text{II}})\text{poly-I}$ film is thermodynamically incapable of mediating the reduction of the outer $(\text{Ru}^{\text{III}})\text{poly-IV}$ film. Furthermore, since these $(\text{Ru}^{\text{III}})\text{poly-IV}$ sites are isolated from the Pt electrode by the inner poly-I film, no reduction wave for the outer poly-IV film is observed. The outer film sites remain trapped in the Ru^{III} state. As a consequence the prewave associated with the catalytic oxidation of the outer poly-IV film is greatly attenuated or entirely absent²⁶ in a subsequent anodic potential scan cycle (dashed curve, Figure 3B). These events demonstrate that electron transfer across the interface between the two polymer films of the bilayer is unidirectional (i.e., rectifying) for the outer, poly-IV ruthenium sites, mimicking an *n*-type semiconductor.

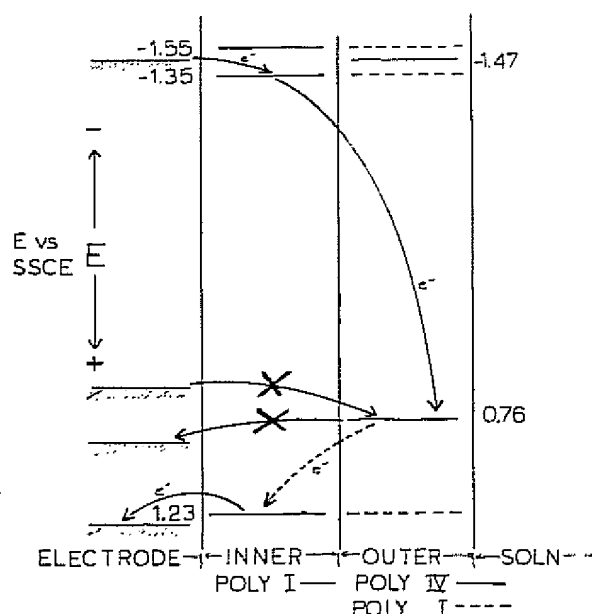
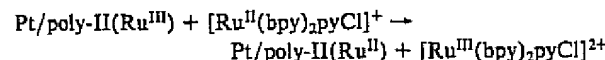


Figure 4. Schematic energy level diagrams for bilayer electrode Pt/poly-I/copoly-I,IV, showing the electron-transfer events of Figure 3.

Some of the most interesting potentialities of bilayer (or multilayer) modified electrodes arise from the manner in which trapped states are released. In the above experiment, trapped Ru^{III} sites in the outer poly-IV film in principle can be released by (i) exposure to a CH_3CN solution of monomer IV or other suitable reductant, (ii) scanning the electrode potential negatively to the bpy-localized reduction of poly-I, (iii) photogeneration of $(\text{Ru}^{\text{III}}, \text{bpy}^-)\text{poly-I}$ excited states in the inner and outer film with subsequent electron-transfer quenching by trapped $(\text{Ru}^{\text{III}})\text{poly-IV}$ sites, or (iv) electrolysis by a second working electrode in contact with the outer film. We have demonstrated trapped-site release for i and ii. For ii, Figure 3C shows a negative-going potential scan in which trapped $(\text{Ru}^{\text{III}})\text{poly-IV}$ sites become reduced in a sharp catalytic prewave (potential g) by $\text{Ru}^{\text{II}}, \text{bpy}^-$ sites generated in the poly-I film, analogous to the anodic catalytic prewave. An anodic potential scan following procedure i or ii quantitatively repeats the first scan result of Figure 3B. Note that in the bilayer Pt/poly-I/copoly-I,IV electrode, the normally reversible $\text{Ru}^{\text{III/II}}$ reactions of IV now occur in sharp oxidation and reduction peaks separated by a potential of 2.2 V. Also notable is that, at -1.0 V, trapped $(\text{Ru}^{\text{III}})\text{poly-IV}$ sites in the outer layer are still not released even though the total potential drop across the inner layer, between the electrode and the $(\text{Ru}^{3+/2+})\text{poly-IV}$ outer-layer electron level, can be estimated at ca. 10^5 V/cm .²⁷

Essential to the functioning of the bilayer scheme is the ability of the inner layer to electrocatalytically oxidize (or reduce) species at its outer boundary. We have demonstrated this directly with one-layer Pt/poly-I and Pt/poly-II electrodes in solutions of $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{pyCl}]^+$, whose normal oxidation wave at $E_{\text{ox}}^{\text{II}} = +0.79 \text{ V}$ vs. SSCE is suppressed by the polymer but occurs concurrently with the film's $\text{Ru}^{\text{III/II}}$ wave at +1.2 V. The reaction



proceeds at the film's outer boundary just as in the bilayer electrode above. Reduction of the cation *N,N'*-dimethyl-4,4'-bipyridinium (methylviologen) is also suppressed at Pt/poly-II electrode surfaces, which shows that the polymer films are free from significant pinholes. This is important in preparing bilayer films whose inner layers are not "leaky". This result also demonstrates charge exclusion of cations by the anion-exchange

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(23) In Figure 3A, $E_{\text{red}}^{\text{II}} = +1.23$ and $+0.76 \text{ V}$ vs. SSCE as compared to $E_{\text{red}}^{\text{II}} = +1.24$ and $+0.76 \text{ V}$ for monomers I and IV, respectively. These electron transfers presumably occur via electron hopping between like neighbor complex sites and so extreme dilution of one site with the other may impede reactions of the dilute sites.

(24) $\Gamma_{\text{poly-I}} = 1.5 \times 10^{-4}$ (inner) + 1.3×10^{-4} (outer); $\Gamma_{\text{poly-IV}} \approx 1.3 \times 10^{-4}$ (outer) mol/cm².

(25) A preliminary theory has been developed which accounts qualitatively for the shape and sweep-rate dependence of the sharp prewave, in which the inner polymer layer is considered to be under Nernstian control with electron transfer between inner and outer layers taking place through a second-order chemical step. The rate of this reaction and its associated current thus increase as the inner layer is oxidized and fall off as the outer layer is depleted. P. Denisevich, University of North Carolina unpublished results, 1980.

(26) This results if the potential scan is repeated within a few minutes; background-electron-transfer reactions or bilayer imperfections otherwise slowly discharge trapped Ru^{3+} in poly-IV.

(27) Most of this potential drop actually occurs over the much thinner electrode/inner film double layer.

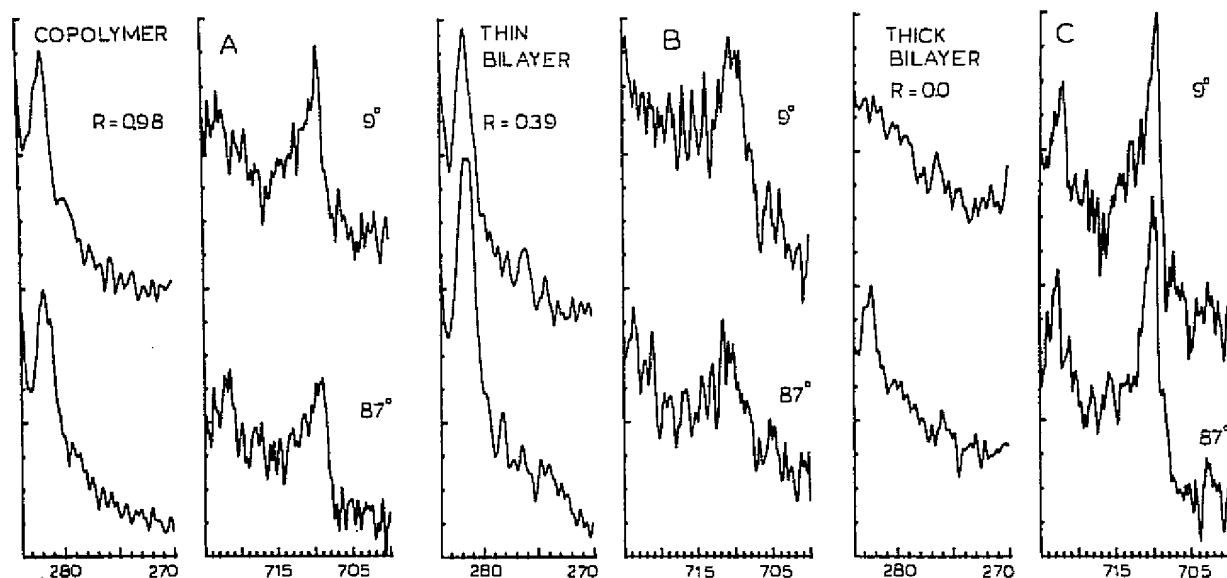


Figure 5. X-ray photoelectron spectra as a function of emission angle θ for Ru $3d_{5/2}$ (BE = 281 eV) and Fe $2p_{3/2}$ (BE = 710 eV) sites in one-layer copolymer Pt/copoly-II,V and bilayer Pt/poly-II/poly-V electrodes, where the poly-V film thickness d for the right-hand bilayer specimen is ca. $3\times$ that of the middle bilayer. Intensity ratio numbers given as $R = [\text{Ru } 3d_{5/2}/\text{Fe } 2p_{3/2}]_{9^\circ}/[\text{Ru } 3d_{5/2}/\text{Fe } 2p_{3/2}]_{87^\circ}$ are (i) independent of θ for copolymer and (ii) smaller for larger d .

polymer films, which is important in avoiding intrusion of cationic monomer IV into the inner film during its polymerization in the bilayer film preparation.

The bilayer scheme for the Pt/poly-I/copoly-I,IV electrode is schematically presented in Figure 4 to emphasize the events discussed above. The essential criteria for successful operation of a bilayer-modified electrode are (i) the inner layer should insulate the outer layer from the electrode at all electrode potentials except those whereby redox reactions of the inner layer occur, which are placed so as to mediate electron transfer between the electrode and outer layer, (ii) the outer layer should be permeable to counterion flow demanded by the redox reactions of the inner layer, (iii) there should be minimal overlap of energy distributions of redox levels of inner and outer polymer film components, and (iv) for repetitive rectification events, release of trapped outer states should be feasible by one or more of the four procedures outlined above. These criteria are well satisfied in Figure 4.

Overlap of the energy distribution functions of inner- and outer-film redox states has a strong bearing on the lifetime of trapped outer-film states. For instance, the difference in $E_{\text{surf}}^{\text{red}}$ of poly-II and poly-V is 0.10 V, as compared to the 0.47-V difference for poly-I and poly-IV. Thus, in a bilayer electrode made from II and V, Pt/poly-II/poly V, the first scan cyclic voltammetry is quite similar to Figure 3B, but on a second anodic potential scan cycle the sharp prewave for (Ru^{III})poly-II inner-film mediated oxidation of outer-film (Fe^{II})poly-V is only mildly suppressed. In the interval between the two scans, the distribution function overlap of (Ru^{II})poly-II and (Fe^{III})poly-V states has allowed the latter trapped states to slowly leak away. We have observed the behavior of additional polymer bilayer films to confirm that the magnitude of the difference in $E_{\text{surf}}^{\text{red}}$ between the bilayer components is important in the perfection of the trapping process. For instance,

a bilayer film made by evaporatively coating a Pt/poly-II electrode with a film of polyvinylferrocene can trap ferricenium outer layer states²⁸ for periods well in excess of 30 min without significant decay.

In the interest of directly demonstrating the bilayer spatial distribution of Ru and Fe sites in a Pt/poly-II/poly-V bilayer electrode, we have measured the relative X-ray photoelectron intensities from these sites as a function of emission angle (θ) relative to the surface plane²⁹ (Figure 5). Attenuation of poly-II Ru 3d photoelectrons by the poly-V film (of thickness d) depends exponentially on $d/\sin \theta$, so that in the spatially segregated bilayer film the intensity ratio for Ru 3d/Fe 2p photoelectrons decreases³⁰ substantially at low angle ($\theta = 9^\circ$) as compared to high angle ($\theta = 87^\circ$). In contrast and as ideally expected, the Ru 3d/Fe 2p intensity ratio is independent of θ for a randomly site-mixed copolymer Pt/copoly-II,V electrode.

These results are presented as supporting a scheme of rectifying and charge-trapping behavior for bilayer-modified electrodes which should be extendable to additional applications, including electrodes mimicking Zener diodes, transistors, optical switches, and solar collectors, among others. Experiments on such extensions will be described in future reports.

Acknowledgment. This research was supported in part by grants from the National Science Foundation and the Office of Naval Research. This is No. 27 in a series of Chemically Modified Electrodes.

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(30) The effect of angle θ is enhanced for a thicker poly-V film (compare Figure 5B,C), as expected for bilayer Ru/Fe site segregation.

Electropolymerization of Ruthenium Bis(1,10-phenanthroline)(4-methyl-4'-vinyl-2,2'-bipyridine) Complexes through Direct Attack on the Ligand Ring System

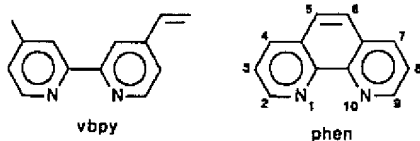
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Mixed ligand complexes of the general type $\text{RuP}_2(4\text{-methyl-4'-vinyl-2,2'-bipyridine})^{2+}$ (where P represents phenanthroline or a substituted phenanthroline) undergo rapid electropolymerization following initial two-electron reduction. The polymerization yields redox-conductive electrode coatings and appears to proceed via radical-radical coupling between the vinyl moiety and a phenanthroline carbon, with the 4- and 7-positions of the phenanthroline being the most reactive. When the phenanthroline ligands possess substituents in the 4- and 7-positions, polymerization still proceeds, but an unexpected reversible electrochemical response near -0.2 V vs. SSCE is generated. The response is attributed to an intermediate which can exist in a stable ligand-centered free-radical form. This radical species has been observed by EPR spectroscopy and is stabilized by 4,7-disubstitution and/or the presence of proton donors. The mechanistic pathways involved in the electropolymerization are complex and lead to multiple products. Polymerized films display unusual electrochemistry, including prominent "charge-trapping" peaks for which a mechanistic system is proposed.

The reductive electropolymerization of ruthenium(II) tris(4-methyl-4'-vinyl-2,2'-bipyridine) ($\text{Ru}(\text{vbpy})_3^{2+}$) and related complexes has received extensive recent study, primarily by Murray and co-workers.¹⁻¹² Electrochemical reduction of these complexes produces polymers that adhere strongly to the electrode surface to form stable electroactive coatings. Electrode coatings produced by this technique have been used to examine electron-transfer kinetics at the film-solution interface^{7,8} and to demonstrate several interesting bistable switching devices.⁹⁻¹² Revealing work of Calvert et al.⁶ suggested that the polymerization proceeds via several pathways, the most important of which is a radical-radical coupling process involving pairs of vinyl groups. This has two important consequences. First, the dominant pathway leads to products with saturated, four-carbon-atom links between the aromatic ring systems. Second, mixed ligand complexes containing only one vinylbipyridine ligand are much less active in the formation of coatings, presumably because, as with activated olefins,^{13,14} end-to-end, radical-radical coupling of two vinyl moieties produces only dimeric products that are soluble in the solvents employed.

To the extent that the 5-6 bond in 1,10-phenanthroline (phen) can be regarded as structurally analogous to the vinyl group in vbpy, one might expect unsubstituted phenanthroline complexes of Ru(II) to undergo reductive electropolymerization in a manner similar to Ru(II) complexes of vbpy. Although direct phen-phen



coupling apparently does not occur, we wish to report that vbpy-phen coupling is efficient, and mixed ligand complexes of the general type $\text{RuP}_2(\text{vbpy})^{2+}$ (where P is a phenanthroline or a substituted phenanthroline ligand) can be rapidly polymerized via electrochemical reduction. One advantage of these mixed ligand complexes is the greater flexibility available in ligand substitution, allowing for variation in parameters such as size, redox potential, and excited-state properties.^{15,16} In addition, since the expected products have two methylene groups separating the aromatic ring system, the rates of charge transport through the redox polymer products may be higher than those obtained with the previous polymers based on $\text{M}(\text{vbpy})_3^{2+}$ ($\text{M} = \text{Ru}, \text{Os}$) complexes.⁶

Experimental Section

Materials. The ligands 5-chloro-1,10-phenanthroline (5-Clphen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me₂phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me₂phen), 4,7-diphenyl-1,10-phenanthroline (4,7-Ph₂phen), and 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-Me₄phen) were obtained from the G. F. Smith Chemical Co. and were used as received. 1,10-Phenanthroline (phen) (Baker) and 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy) (Aldrich) were also used as received. Ruthenium trichloride was obtained from several sources (Aesar, Aldrich, Alfa) and was used without further purification in all cases. Ammonium hexabromooximate was prepared from OsO_4 (Aldrich) by using standard literature methods.¹⁷ Tetra-*n*-butylammonium perchlorate (Southwestern Analytical) and sodium perchlorate (Aldrich) were recrystallized twice and dried overnight in a vacuum oven. Acetonitrile (Burdick and Jackson UV) was distilled from CaH_2 prior to use.

4-Methyl-4'-vinyl-2,2'-bipyridine (vbpy). This ligand was prepared by a slight modification of the method of Spiro and

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* Contribution No. 7502.

Ghosh.¹⁸ First, 25 mL of 2.6 M *n*-BuLi (Aldrich) was carefully added to a solution containing 4 mL of diisopropylamine (Aldrich) in 15 mL of dry tetrahydrofuran (THF). The resulting mixture was stirred for 15 min. A solution of 5.0 g of Me₂bpy in 125 mL of dry THF was then slowly added via a dropping funnel to produce an orange-brown solution. A stream of formaldehyde, prepared by passing dry argon over 2.0 g of paraformaldehyde in a heated flask (~50 °C), was bubbled through the solution for 2 h. The reaction was then quenched with ice water and extracted with ether. Most of the solvent was removed from the organic layer, and the resulting yellow oil was filtered to remove any unreacted Me₂bpy. The product, 4-CH₃-4'-CH₂CH₂OH-bpy, was purified by column chromatography on deactivated alumina with ethyl acetate as the eluant. Dehydration was achieved by adding ~0.5 g of powdered NaOH to the oil in a vacuum sublimator and heating the mixture to 130 °C under vacuum. The product, vbpy, was collected as a white crystalline solid on the cold finger.

RuP₂Cl₂ (Except Ru(3,4,7,8-Me₄phen)₂Cl₂). These compounds were prepared by using the method of Sprintschnik et al.¹⁹

Ru(3,4,7,8-Me₄phen)₂Cl₂. This compound proved difficult to prepare by the method of ref 19 and was synthesized by the following procedure: 203 mg of RuCl₃·3H₂O (0.78 mmol) was added to 50 mL of ethanol and briefly refluxed to facilitate dissolution. 3,4,7,8-Me₄phen, 370 mg (1.57 mmole), was added along with a fivefold excess of hydroxylamine hydrochloride to serve as a reducing agent. After 1 h of refluxing, the reddish-orange solution was cooled and filtered. The filtrate was concentrated and passed down a Sephadex LH-20 column using 2:1 MeOH/DMF as eluant. The chloride salt was obtained by addition of aqueous LiCl, followed by removal of methanol and overnight refrigeration.

RuP₂(vbpy)(PF₆)₂. These compounds were prepared by refluxing stoichiometric amounts of vbpy with the appropriate RuP₂Cl₂ complex in methanol for 3 h. Purification was achieved by column chromatography on Sephadex LH-20 using either methanol or 1:1 MeOH/DMF as eluant. The hexafluorophosphate salts were obtained by addition of aqueous NH₄PF₆ to a methanolic solution of the complex, followed by slow removal of the methanol under vacuum. The resulting products were usually either crystalline or microcrystalline and were characterized by NMR and elemental analyses.

Os(phen)₂Br₂. (NH₄)₂OsBr₆ (605 mg, 0.86 mmol) and 1,10-phenanthroline (340 mg, 1.72 mmol) were refluxed for 1 h in 20 mL of dimethylformamide (DMF). The solution was cooled and 50 mL of MeOH was added. Addition of 70 mL of dilute Na₂S₂O₄ produced a black precipitate, Os(phen)₂Br₂, which was recrystallized from CHCl₃ (yield: 534 mg, 88%).

Os(phen)₂(vbpy)(PF₆)₂. Os(phen)₂Br₂ (321 mg, 0.45 mmol) and vbpy (100 mg, 0.51 mmol) were dissolved in 40 mL of 5:1 H₂O/EtOH and refluxed for 3 days. The mixture was filtered, and the product was precipitated by the addition of aqueous NH₄PF₆ to the filtrate. The complex was purified by column chromatography on Sephadex LH-20 (1:1 MeOH/DMF) (yield: 313 mg, 67%).

Procedures. Electrochemical measurements were performed with a Princeton Applied Research Model 173 potentiostat, a Model 175 universal programmer, and a Model 179 digital coulometer. The glassy carbon electrodes were prepared by polishing small lengths of 5- or 6-mm-diameter GC-20 rod (Tokai) with wetted sandpaper, then with successively finer alumina (Buehler 3.0, 1.0, and 0.3 μm). The electrode was cleaned in an ultrasonic bath between each step to remove any adhering particles. Heat-shrinkable polyolefin tubing (Alfa Wire Co.) was used to attach the short carbon rods to glass tubing so that only the polished surface was exposed to the solution. Electrical contact was made to the back of the rod by means of a small Hg pool and a copper lead. Regeneration of the electrode surface between

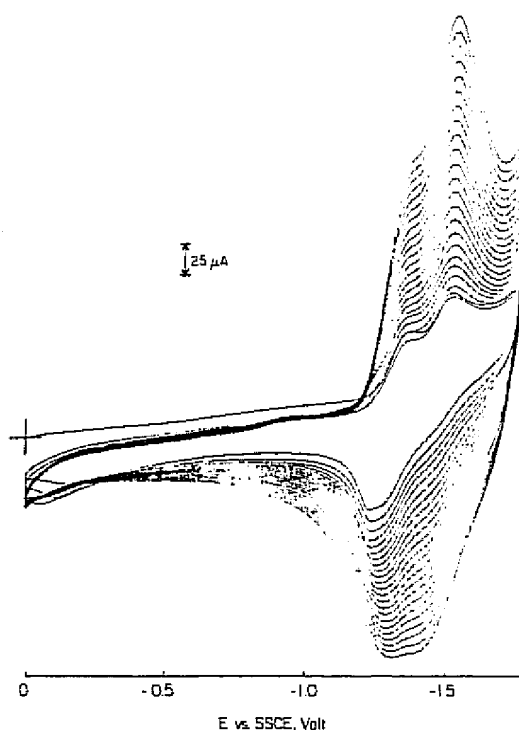


Figure 1. Cyclic voltammograms recorded continuously at 100 mV s⁻¹ with 0.4 mM [Ru(phen)₂(vbpy)]²⁺ in acetonitrile. Glassy carbon electrode (0.2 cm²). Supporting electrolyte: 0.1 M NaClO₄.

experiments was accomplished by repeating the 0.3-μm polishing (0.3-μm alumina) and ultrasonic cleaning steps. No major differences in electrode behavior were observed when commercially available, premounted glassy carbon electrodes [Bioanalytical Systems, Inc.] were employed. Electrode potentials were measured and are quoted with respect to a sodium chloride saturated calomel electrode (SSCE).

Samples for electron spin resonance (ESR) experiments were prepared by electropolymerization of the desired complex onto a coiled Pt wire which served as the working electrode. Typically, the Pt wire was cycled continuously at 50 mV/s from 0 to 1.8 V vs. SSCE in a 0.5 mM solution of the complex in acetonitrile containing 0.1 M NaClO₄ as supporting electrolyte. After coating, the electrode was removed, rinsed with dry acetonitrile, and dried in a standard ESR tube under vacuum. The tube was then placed in the cavity and the ESR signal measured in the absence of solvent. Spectra were recorded on a Varian E-line Century Series X-band spectrometer operating in the absorption mode.

Results

A series of cyclic voltammograms recorded during the reductive electropolymerization of Ru(phen)₂(vbpy)²⁺ is shown in Figure 1. The continuous increase in the peak currents of the waves at -1.4 and -1.55 V results from accumulation of an electroactive polymer on the electrode surface. As with the polypyridine complexes described in previous studies,¹⁻¹² the deposition of polymer on the electrode is more rapid when the electrode potential is scanned over both of the reduction waves. Five additional Ru complexes and one Os complex, each containing two phenanthroline-based ligands and one vbpy ligand, were also electropolymerized in a similar fashion. These complexes and the formal potentials of the monomers and their polymeric products are listed in Table I. The reactivity of the M(phen)₂(vbpy) complexes contrasts sharply with that of the much less reactive M(bpy)₂(vbpy) analogues, which suggests that the reduced vbpy ligand may attack the phenanthroline ring system. It should be noted that Ru(phen)₂²⁺ does not electropolymerize under these conditions, so that coupling between phen ligands on reduced complexes apparently does not occur at an appreciable rate.

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TABLE I: Formal Potentials of $\text{RuP}_2(\text{vbpy})^{2+}$ Monomers and Reductively Electropolymerized Polymers^a

P	monomer			polymer		
	$E_{3+/2+}$	E_1	E_2	$E_{3+/2+}$	E_1	E_2
phen	+1.22	-1.33	-1.51	+1.20	-1.30	-1.53
5-Clphen	+1.24	(-1.29) ^b	c	+1.18	~-1.38	-1.60
5,6-Me ₂ phen	+1.12	(-1.44) ^b	-1.62	+1.11	-1.41	-1.60
4,7-Ph ₂ phen ^e	+1.13	-1.38	-1.53	+1.14	-1.32	-1.49
4,7-Me ₂ phen	+1.08	-1.44	-1.66	+1.08	-1.48	-1.66
3,4,7,8-Me ₄ phen	+1.02	-1.47	c	+1.04 ^d	-1.51	-1.69
phen ^f	+0.72	-1.34	-1.52	+0.70	(-1.33) ^c	-1.52

^a Formal potentials are the average of cathodic and anodic peak potentials measured at a scan rate of 100 mV s⁻¹ at a glassy carbon electrode in CH₃CN with 0.1 M NaClO₄ as supporting electrolyte. $E_{3+/2+}$ corresponds to the M(III)/M(II) couples. E_1 and E_2 correspond to the first and second, ligand-centered, ^{6,15,20,21} reductions of the M(II) complex. ^b Adsorption of reduced material made measurement of the anodic peak potential imprecise. ^c Irreversible. ^d Second, smaller couple also present at +1.24 V. ^e Ph = phenyl. ^f Osmium(II) complex.

Estimates of the relative rates of the polymerization reactions can be obtained from the increase in charge consumed on successive reductive scans. The results of such measurements show that the rate of deposition obtained with the complexes listed in Table I is approximately the same except for Ru(4,7-Ph₂phen)₂(vbpy)²⁺ which polymerizes much more slowly than the other six complexes. In fact, in DMF, no evidence for polymerization of this complex was observed, even after 60 min of continuous cycling. (All of the other complexes did electropolymerize in DMF, although their rates of polymerization were much lower than in acetonitrile.) This difference in reactivity needs to be accommodated by schemes proposed for the electropolymerization. Additional evidence useful for constructing a reaction scheme was obtained from the behavior of the Ru(3,4,7,8-Me₄phen)₂(vbpy)²⁺ complex. For this complex, the two cathodic waves corresponding to the reduction of the vbpy and Me₄phen ligands, respectively, ^{15,20,21} are well separated. The first appears near -1.5 V and the second near -1.8 V. When the electrode is cycled between 0 and -1.6 V vs. SSCE, i.e., just beyond the peak for the reduction of the vbpy ligand, very little electropolymerization results. However, if the negative potential range is extended to -1.8 V, i.e., to the middle of the Me₄phen reduction wave, the polymerization proceeds at a much higher rate (Figure 2). Evidently reduction of both the vbpy and the Me₄phen ligands is necessary for rapid polymerization. Thus, it appears that radical or anionic chain growth pathways, which would require only a single reduced ligand, are relatively unimportant. A similar line of reasoning has been employed in arriving at a proposed mechanism for the electropolymerization of Ru(vbpy)₃²⁺ complexes.⁶

Three of the complexes yield polymers that display an unusual feature in their electrochemical responses. During electropolymerization of Ru(4,7-Me₂phen)₂(vbpy)²⁺, Ru(4,7-Ph₂phen)₂(vbpy)²⁺, and Ru(3,4,7,8-Me₄phen)₂(vbpy)²⁺, a very prominent, reversible response develops in the region between -0.1 and -0.3 V vs. SSCE (Figure 2). This response is surprising because the corresponding monomeric complexes exhibit no electrochemical activity in this potential region. Electropolymerized coatings that exhibit this unusual reversible response are blue rather than orange, the color obtained with the other Ru complexes. In aprotic solvents, the behavior is limited to complexes with substituents in the 4- and 7-positions. However, if the electropolymerizations are carried out in the presence of water, mineral acids, ammonium ions, or other proton donors, complexes with or without substituents in the 4- and 7-positions develop the same voltammetric response (see Figure 3) and yield blue instead of orange coatings. Depending on the exact conditions employed, the voltammetric responses in the potential region near -0.2 V can appear as a single

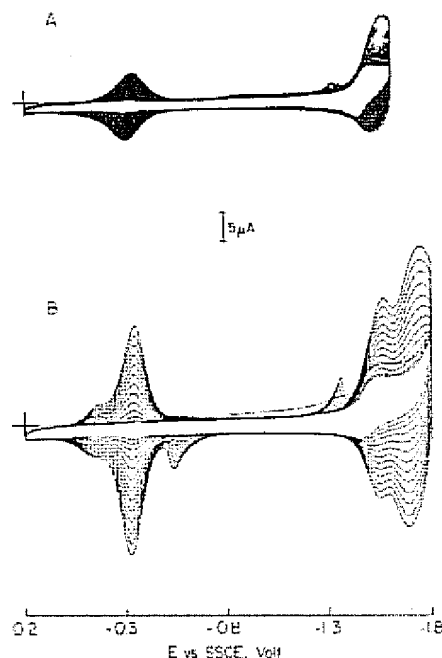


Figure 2. Cyclic voltammograms recorded continuously with 0.24 mM $[\text{Ru}(3,4,7,8\text{-Me}_4\text{phen})_2(\text{vbpy})]^{2+}$. Glassy carbon electrode (0.07 cm²). Other conditions as in Figure 1. (A) 75 cycles at potentials between +0.2 and -1.6 V; (B) 13 cycles between +0.2 and -1.8 V.

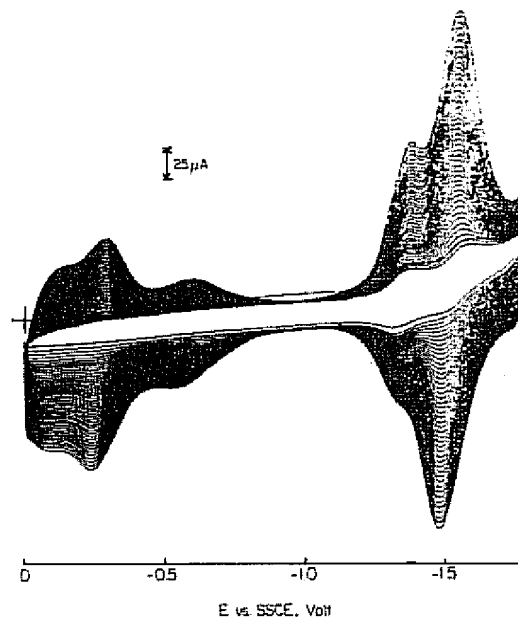


Figure 3. Continuously recorded cyclic voltammograms for 0.2 mM $[\text{Ru}(5,6\text{-Me}_2\text{phen})_2(\text{vbpy})]^{2+}$. Supporting electrolyte: 0.1 M NaClO₄ + 0.1 mM HClO₄. Other conditions as in Figure 1.

reversible couple, as several well-defined reversible couples separated by several hundred millivolts, or as a broad, featureless wave. The behavior suggests that several different species and/or local environments may be involved.

The reversible response near -0.2 V remains relatively stable as long as the potential is not scanned to values more positive than ca. +1.4 V. However, a single scan of the potential to +1.5 V and back causes the response near -0.2 V to disappear, presumably because of an irreversible oxidation of the species responsible for the response. Consistent with this explanation is the fact that an irreversible oxidation peak, located slightly positive of the peak for the reversible oxidation of Ru(II) to Ru(III), is often observed on the first scan to +1.5 V and is absent on subsequent scans.

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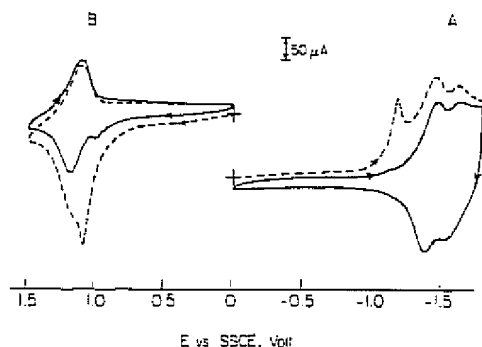


Figure 4. Cyclic voltammograms of a coating containing a mixture of two complexes. The coating was prepared by cycling the potential of a glassy carbon electrode (0.2 cm^2) between 0 and -1.8 V at 100 mV s^{-1} for several minutes in an acetonitrile solution containing 0.1 M NaClO_4 and 0.3 mM of both $\text{Ru}(\text{vbpy})_3(\text{PF}_6)_2$ and $\text{Os}(\text{phen})_3(\text{PF}_6)_2$. The coated electrode was washed and transferred to a pure supporting electrolyte solution to record the voltammograms shown. (A) Potential scanned between 0 and -1.8 V : solid line, steady response obtained with unoxidized coating; dashed line, initial response obtained after coating had been cycled to $+1.5 \text{ V}$. (B) Potential scanned between 0 and $+1.5 \text{ V}$: dashed line, initial response obtained with unoxidized coating; solid line, steady response obtained with oxidized coating.

Coatings of Mixed Complexes. The attack of reduced vbpy radical anion ligands on reduced phenanthroline ligands is a general reaction that introduces the possibility of preparing mixed complexes. For example, reduction of an equimolar mixture of $\text{Ru}(\text{vbpy})_3^{2+}$ and $\text{Os}(\text{phen})_3^{2+}$ at a transparent SnO_2 electrode produces a coating that contains both ruthenium and osmium complexes as determined by UV-vis spectrophotometry. The $\text{Os}(\text{phen})_3^{2+}$ centers appear to be covalently bound and not simply physically encapsulated by the polymer because $\text{Os}(\text{bpy})_3^{2+}$ is not incorporated under identical conditions.

Interestingly, the $\text{Os}(\text{phen})_3^{3+/2+}$ couple is not observed in cyclic voltammograms of electrodes coated with the mixed polymer. This result can be rationalized by considering the likely polymer structure: Reduced phenanthroline ligands can react with reduced vinylbipyridine ligands but not with each other, so that the Os metal centers will have only Ru sites as nearest neighbors. On the other hand, the reduced vinylbipyridine ligands can couple with each other as well as reduced phenanthroline ligands so that the Ru sites in the polymer can have both Os and Ru neighbors. Since electron transport in these films is believed to occur via electron exchange between neighboring oxidized and reduced sites, the structure of the mixed complex coatings prevents oxidation of the Os(II) sites near the $\text{Os}(\text{phen})_3^{3+/2+}$ potential. However, the Os(II) sites should be oxidizable by cross-reaction with Ru(III) sites that are generated at more positive potentials.

In Figure 4 are shown cyclic voltammograms for a mixed coating that are consistent with this interpretation. The steady, irreversible response at potentials near -1.4 V (solid line) arises from the Ru complexes in the coating. If the electrode potential is scanned to positive values where Ru(III) is generated (Figure 4B, dashed line), a large anodic peak is obtained on the first but not subsequent scans (Figure 4B; solid curve). The large magnitude of the peak results from the Ru(III)-mediated oxidation of the Os(II) centers. The resulting Os(III) centers are not reduced directly during the return scan because Ru(II) cannot reduce Os(III). A corresponding cathodic peak appears on the first subsequent scan to more negative potentials (Figure 4A, dashed curve) where the Os(III) centers are reduced by cross-reaction with the reduced Ru(II) complex. The enhanced anodic and cathodic peaks are present at the same positions during every scan if the range of the potential scan is expanded to $+1.5$ to -1.8 V .

"Charge-trapping spikes" similar to those in Figure 4 have been previously described and analyzed by Murray and co-workers in the case of bilayer coatings where the reactants giving rise to the enhanced current peaks are contained in an outer layer of the coating that makes electronic contact with the electrode only via

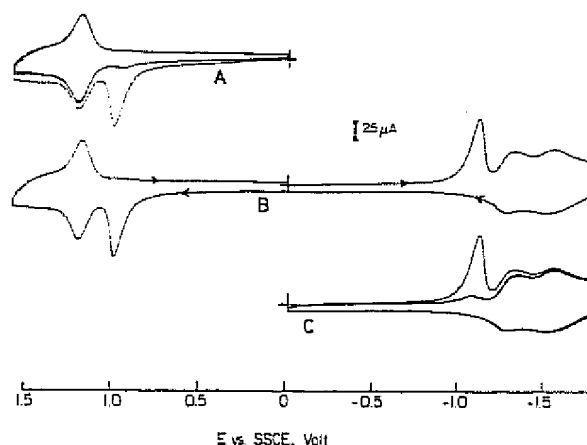


Figure 5. Cyclic voltammograms for an electropolymerized coating prepared by cycling a glassy carbon electrode (0.07 cm^2) between 0 and -1.8 V for several minutes in 0.3 mM $[\text{Ru}(\text{phen})_2(\text{vbpy})]^{2+}$. Potential scanned between (A) 0 and $+1.5 \text{ V}$, anodic charge-trapping spike present only on first scan; (B) $+1.5$ and -1.8 V , charge-trapping spikes present in every scan; (C) 0 and -1.8 V , cathodic charge-trapping spike present only on first scan. Other conditions as a Figure 1.

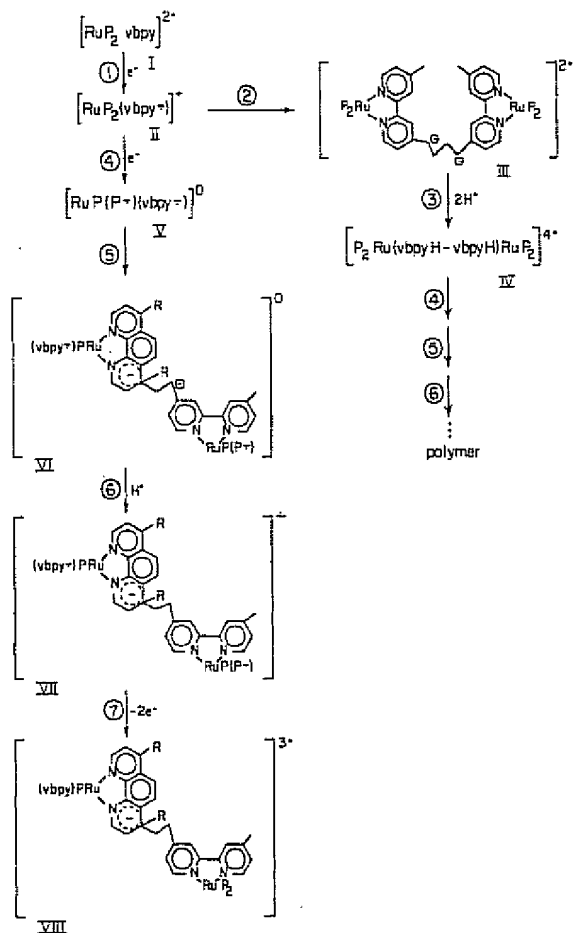
the inner layer.⁹⁻¹² In the present case, the Os(III)/(II) centers responsible for the charge-trapping spikes are distributed uniformly throughout a single layer and their charge-trapping behavior results from the chemistry responsible for the deposition of the polymeric coatings that forces the Os centers to be surrounded by Ru centers.

All electroactive species that were dispersed throughout a polymeric $\text{Ru}(\text{vbpy})_3^{2+}$ coating in a way that prevented uninterrupted direct electronic pathways to the electrode surface would be expected to show behavior similar to that in Figure 4 if their formal potentials were between those where the $\text{Ru}(\text{vbpy})_3^{2+}$ centers are oxidized ($+1.0 \text{ V}$) and reduced (-1.3 V). This fact may help to explain the otherwise surprising observation that charge-trapping spikes are sometimes observed with single-component coatings. For example, coatings prepared by reductive electropolymerization of $\text{M}(\text{phen})_2(\text{vbpy})$ complexes behave similarly to the mixed Ru-Os coatings (Figure 5), although no "trappable" species were intentionally introduced. Evidently, the reaction sequence involved in the electropolymerization produces some isolated sites with formal potentials between $+1.0$ and -1.3 V . It may be that the electrogenerated species that gives rise to the reversible voltammetric responses shown in Figures 2 and 3 may also be formed at sites that lack a direct pathway to the electrode so that their existence is only evident from the charge-trapping responses they produce. The observed behavior suggests that the use of complexes containing 4,7-substituted phenanthrolines and/or the presence of proton donors favors the production of untrapped species with formal potentials near -0.2 V while the generation of trapped species is more common in the absence of 4,7-substituents or proton donors.

Discussion

On the basis of the results we have described, a possible reaction sequence to account for the reductive electropolymerization of $\text{RuP}_2(\text{vbpy})_3^{2+}$ complexes (where P represents a phenanthroline-based ligand) can be proposed (Scheme 1). After an initial one-electron reduction (reaction 1, Scheme 1), dimerization could occur via radical-radical coupling of the vinyl moieties (reaction 2), followed by rapid protonation of the coupled product (reaction 3).^{6,13,14} However, such vinyl-vinyl coupling is relatively inefficient^{6,13,14} so that most of the singly reduced monomer (II) is likely to survive long enough to undergo a second one-electron reduction at the electrode^{6,13,14} (reaction 4) to yield a complex containing a pair of reduced ligands. An alternative type of radical-radical coupling can now occur, in which a reduced vinyl group on one complex attacks the reduced phenanthroline ring of a second complex (reaction 5). This facile vbpy-phen radical-radical coupling is the novel feature of the $\text{RuP}_2(\text{vbpy})_3^{2+}$ complexes.

SCHEME I



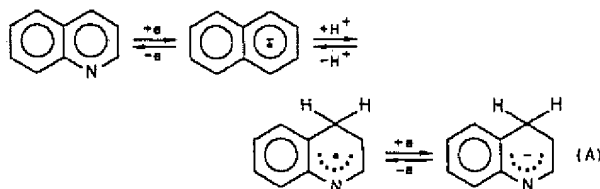
Previously reported examples involved only vinyl-vinyl coupling.⁶ Our results suggest that conventional radical and/or anionic chain growth pathways are inefficient with the $RuP_2(vbpy)_2^{2+}$ complexes because the electropolymerization proceeds very slowly when only a single ligand is reduced. One reason may be that the 2-position, which is the site most susceptible to radical attack in the free ligands,²² is sterically hindered in the coordinated ligands. The radical-radical coupling reaction (reaction 5 in Scheme I) is expected to be much faster^{6,23} than radical or anionic chain growth, and its rate is further enhanced by the high concentration of radicals near the electrode surface.

A similar reactivity pattern is exhibited by both pyridinium and quinoline derivatives, which generally dimerize via 2-2' or 4-4' radical-radical coupling following electroreduction.²⁴⁻²⁷ These precedents, along with the much lower rate of reductive electropolymerization of $Ru(4,7-Ph_2phen)_2(vbpy)^{2+}$, suggest that the coupling involves the 4- or 7-position of the phenanthroline ligand, as depicted in Scheme I. Further evidence implicating the 4- and 7-positions comes from previous photolysis²⁸ and radiolysis²⁹

studies, where free-radical attack on coordinated phenanthroline, initially thought to occur at the 5- or 6-positions,²² was shown to occur at the 4-position.²⁹ Interestingly, and in accord with the present results, the analogous bipyridine complexes are essentially unreactive.²⁹

The coupling reaction depicted in reaction 5 of Scheme I produces a neutral but very basic species that would be expected to extract a proton from extraneous water or from the acetonitrile solvent itself (reaction 6) to produce VII. The reduced vinylbipyridine and phenanthroline ligands in species VII would be reoxidized at potentials near -1.3 V during the scan of the potential to more positive values (reaction 7). The oxidation product, VIII, is analogous to intermediates that are formed in nucleophilic substitution reactions of pyridine with alkyl lithium reagents^{30,31} and with alkali amides (Chichibabin reaction).^{32,33}

Species VIII also resembles the product obtained when quinoline is reduced in nonaqueous solvents.²⁷ This reaction proceeds in the two one-electron steps shown in reaction A. The quinoline



radical anion formed first is rapidly protonated by even traces of water, and the product is easier to reduce than quinoline itself so that a second electron is consumed. Both experimental and theoretical evidence is available^{27a,d} to support assignment of the 4-position in the quinoline molecule as the site of the protonation.

Cyclic voltammograms for the quinoline system exhibit an anodic peak at a potential much more positive than that where the quinoline reduction peak appears.²⁷ The anodic peak is attributable to the reverse of reaction A, which must proceed at the more positive potential required for oxidation of the doubly reduced anion that closely resembles species VIII in Scheme I. Thus, reaction A is reversible, but the cathodic and anodic peak potentials are widely separated.

The assumption that species VIII behaves analogously to the doubly reduced anion of the quinoline system provides a possible explanation for the electrochemical response near -0.2 V in Figures 2 and 3. The reasoning is outlined in Scheme II. The half-reaction for the $RuP_2(vbpy)^{2+}$ system that is analogous to the second electron-transfer step of reaction A is reaction 8 in Scheme II. With the quinoline system, the anodic peak has no cathodic counterpart near the same potential²⁷ while a reversible response near -0.2 V is obtained with the $RuP_2(vbpy)^{2+}$ system. We believe this difference helps to support our interpretation because the presence of substituents in the 4- and 7-positions of the original complex would make it impossible for intermediate IX in Scheme II ($R \neq H$) to deprotonate to form intermediate X. As a result, IX should persist at the electrode surface where it would give rise to a cathodic wave near the same potential where it was formed (half-reaction 8). When the 4- and 7-positions are occupied by hydrogen, intermediate IX ($R = H$) can deprotonate to form X (reaction 9), which would be rapidly oxidized (reaction 10) at the potential where reaction 8 proceeds. However, if reaction 9 were reversible, the presence of excess protons could prevent the deprotonation of IX and thereby result in reversibility for reaction 8, even when $R = H$. This provides an explanation for the ability of added acid to stabilize the reversible response near -0.2 V in Figures 2 and 3.

Further evidence supporting the assignment of the reversible response near -0.2 V in Figures 2 and 3 to reaction 8 in Scheme II was obtained from an EPR experiment: The coating resulting

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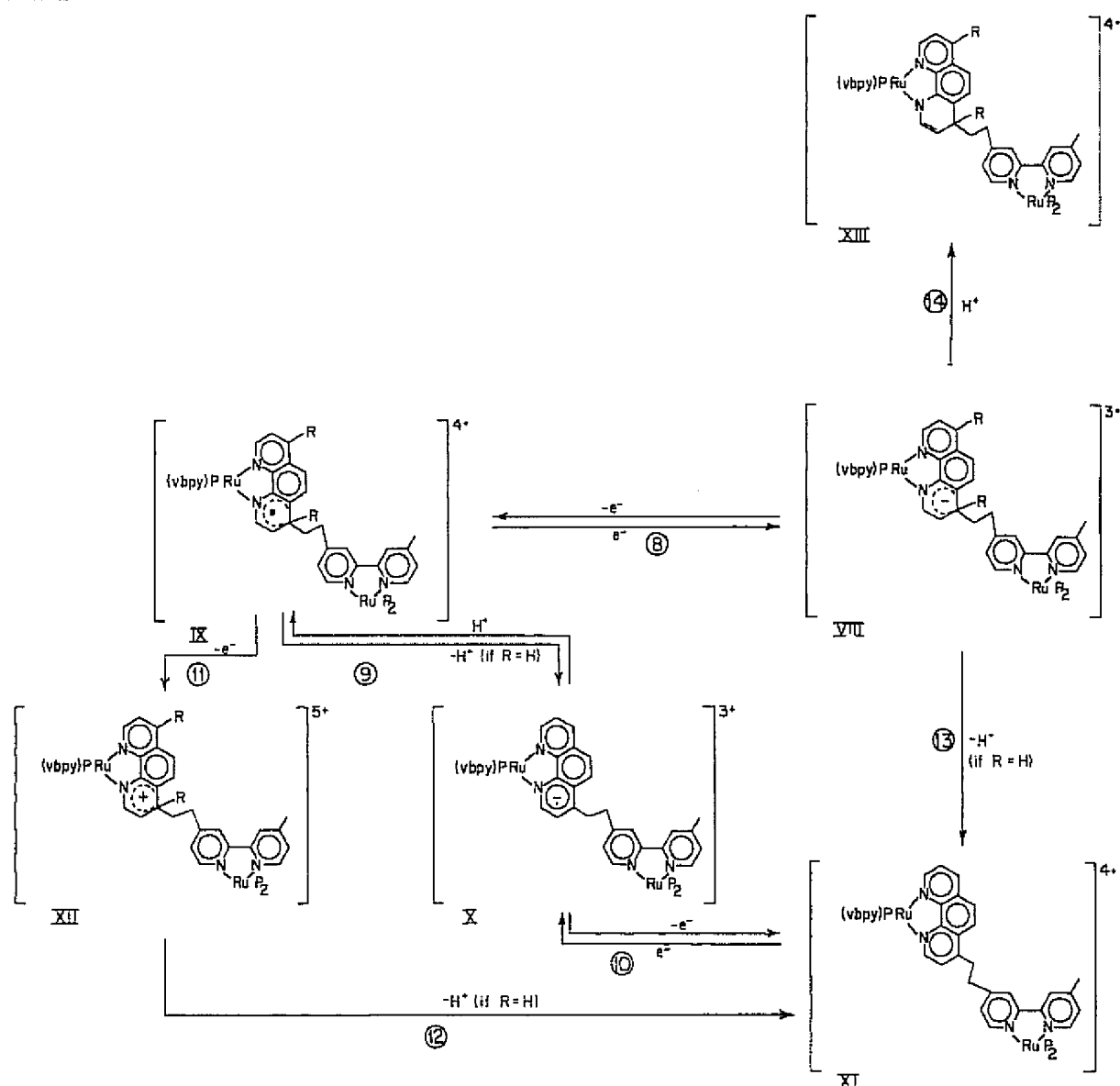
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SCHEME II



from the reductive electropolymerization of $Ru(4,7-Me_2phen)_2-(vbpy)^{2+}$ was maintained for several minutes at +0.2 V where radical IX in Scheme II is expected to be stable. Transfer of the washed and dried film to the EPR spectrometer produced a single-line signal with $g = 2.003$. The signal disappeared if the electrode potential was set between -0.5 and -1.0 V for several minutes before recording the spectrum. The EPR signal could be removed and restored several times (with some loss of intensity) by cycling the electrode potential between +0.2 and -0.8 V. These results indicate that reaction 8 in Scheme II is reversible and that the radical, IX, is apparently fairly stable within the polymeric coating. No hyperfine structure was detected in the EPR spectrum at temperatures as low as 10 K, presumably because of very rapid exchange interactions within the polymer.^{34,35} A Dysonian line shape³⁶ was observed for several samples, even at room temperature, suggesting that the polymeric coatings possess at least some electronic conductivity in the dry state.^{36,37}

In the absence of acid, with complexes where $R = H$, the anodic wave near -0.2 V is present only for the first few scans of the electropolymerization. Apparently, these first few scans produce a thin layer of polymeric material on the electrode surface that interferes with the continued oxidation of VIII via reactions 8-10 in Scheme II. This behavior may result from the following sequence of events: During the cathodic portion of the first cycle, vbpy-phen coupling proceeds as shown in Scheme I (eq 5). The return scan eventually produces intermediate VIII, which undergoes an irreversible oxidation (reactions 8-10 in Scheme II), leading to a layer of polymeric XI on the electrode surface in which the basic ruthenium polypyridine structure remains intact. Thus, since this is a redox polymer, and ruthenium polypyridines are electroinactive between about +1.0 V and -1.3 V, the layer of polymeric XI acts as an electrical insulator in this potential region.⁹⁻¹² Electropolymerization can still proceed, because the necessary reduction of additional monomer in solution occurs at more negative potentials (-1.5 V) where the film is redox-conductive. However, the anodic waves at -0.2 V disappear because the insulating layer next to the electrode surface prevents the

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oxidation of any material in the outer layers at this potential. In essence, a bilayer electrode⁹⁻¹² is produced, with an inner layer consisting of structures such as XI and the outer layer consisting of structures such as VIII.

In cases where radical IX contains no substituents in the 4- or 7-positions of the phenanthroline rings ($R = H$), it may be converted to the final product, XI, by another pathway that depends on the electrode potential. At sufficiently positive potentials, the oxidation of IX (reaction 11, Scheme II) could precede a rapid deprotonation^{38,39} (reaction 12). This second pathway may account for the irreversible oxidation often observed when the potential was swept to +1.5 V. However, the subsequent disappearance of the response near -0.2 V is more difficult to explain because the reverse of reactions 10 and 9 would permit radical IX to be regenerated. This disappearance of the response at -0.2 V following a potential excursion to +1.5 V is not yet understood.

Another feature of these films that is difficult to understand, particularly for the unsubstituted complexes in the absence of acid, is the stability of the prominent charge-trapping peaks. If the complex exists in the radical form (IX) for an appreciable amount of time, deprotonation and oxidation would be expected to occur (eq 9 and 10) leading eventually to a film containing only polypyridine units (structure XI). The charge-trapping peaks should then disappear because the film would consist entirely of one species. However, this is not observed; the trapping peaks are stable to repeated cycling for hours in very dry solvents. The origin of this behavior is unclear. It might indicate that additional species, such as reduced ligand sites (structure XIII), can lead to the appearance of the charge-trapping peaks.

In addition to the one-electron oxidation/reduction depicted in reaction 8 of Scheme II, intermediate VIII can undergo several other reactions. For example, when $R = H$, elimination of hydride from the C-4 position (reaction 13) may proceed to produce a binuclear complex (XI) containing a phenanthroline ligand substituted in the 4-position. Such hydride elimination reactions are well-known in the nucleophilic substitutions of pyridine.^{25,30-33} In the present case, hydride elimination would lead to the same product (XI) that is obtained by the sequence of reactions 8 to 10 or 8, 11, 12 in which the polypyridine ligands that occupy the coordination sphere of the ruthenium remain essentially unperturbed. For this reason, the electrochemical behavior of the polymer coating resulting from either pathway would be expected to mimic that of the monomeric precursor from which it was generated. In fact, the formal potentials of the surface wave for the polymer films match those of the corresponding monomeric complexes (Table I), which indicates that species XI is the major component of the polymeric coatings.

A final pathway available to intermediate VIII involves protonation to yield structure XIII or a related isomer in which the phenanthroline ligand has been partially reduced (reaction 14). The electrochemistry of a polymer coating containing such reduced ligands would be expected to differ significantly from that of the original monomeric complex because the formal potential of the $Ru^{III/II}$ couple would be more negative if one (or more) of the coordinated N atoms became saturated.⁴⁰ Although no such products were observed by the electrochemical methods employed here, their presence could not be precluded. If their concentrations were low, the redox activity of these sites would be evident only through charge-trapping peaks.⁹⁻¹² At present, it is impossible to assess how much, if any, of the charge-trapping behavior that is observed arises from species such as XIII or further reduction products. However, a large contribution from such species might account for the otherwise unexpected stability of the charge-trapping peaks.

Summary and Conclusions

Complexes of the general type $RuP_2(vbpy)^{2+}$ (where P is a phenanthroline-based ligand) have been found to undergo rapid polymerization following two-electron electroreduction. The mechanism of the polymerization appears to involve radical-radical coupling of the vinylbipyridine and phenanthroline ligands, with the 4- and 7-positions of phenanthroline being the most reactive. The coupling process leads to a complicated reaction sequence in which a variety of products are possible, some of which can be interconverted by electrochemical oxidation or reduction. The net result is the deposition on the electrode of an electroactive, redox-conductive film containing several chemically distinct species. The presence of these species can be inferred from charge-trapping peaks and, under favorable conditions, they can be observed directly in cyclic voltammograms of the electrode coatings. In some cases, the electropolymerization apparently produces a bilayer electrode in essentially a single step.

One attractive feature of the coupling reactions described here is their potential utilization in the production of binuclear metal complexes. For example, electroreduction of a mixture of $Ru(bpy)_2(vbpy)^{2+}$ and $Ru(bpy)_2(phen)^{2+}$ would be expected to produce $[(bpy)_2Ru(vbpy-phen)Ru(bpy)_2]^{n+}$. Such chemistry might then be extended to the synthesis of mixed-metal binuclear, trinuclear, and tetranuclear species, as well as electron donor-acceptor complexes. It is clear from the present results that careful control of reaction conditions will be necessary to constrain the reaction sequence to the desired pathway in the face of the numerous alternative possibilities.

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